

CONTRACT SPC-93-4033

6th two-month Progress Report

June-July 1994

Introduction

In this 6th two-month period we have continued the characterization of PMMA-based electrolyte membranes by examining the phenomena occurring at the interface between these membranes and the lithium metal electrode, with the final aim of completing Task III of the Project.

Task (iii) - Synthesis and test of 'new' gel-type lithium electrolytes.

Experimental.

The synthesis of the three representative samples of PMMA-based gel electrolytes considered in this work, namely the systems having the following molar composition:

- S-1) PMMA: 30/PC : 19/EC:46.5/LiClO₄:4.5
- S-2) PMMA: 30/PC : 19/EC:46.5/LiAsF₆:4.5
- S-3) PMMA: 30/PC : 19/EC:46.5/LiN(CF₃SO₂)₂:4.5

and the method used to investigate their stability towards the lithium metal electrode, have been described in the previous 5th two-month Progress Report.

Results.

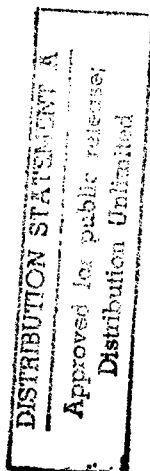
Stability of the lithium electrode interface

In the previous Progress Reports we have demonstrated that PMMA-based and PAN-based electrolytes have very favourable transport and electrochemical characteristics. However, high conductivity, high lithium transport number and wide electrochemical window, although important properties, are not sufficient to make an electrolyte completely useful in practical terms. The compatibility with the electrode materials is also an

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essential parameter to guarantee acceptable performance in electrochemical devices, e.g. batteries, especially when cyclability and reliability are considered. To investigate this crucial aspect and in the attempt of determining the stability of the lithium/PMMA-based electrolyte interface under prolonged time scale, we have carried out a detailed impedance analysis of symmetrical cells of the Li/electrolyte/Li type, stored and tested under open circuit conditions at room temperature.

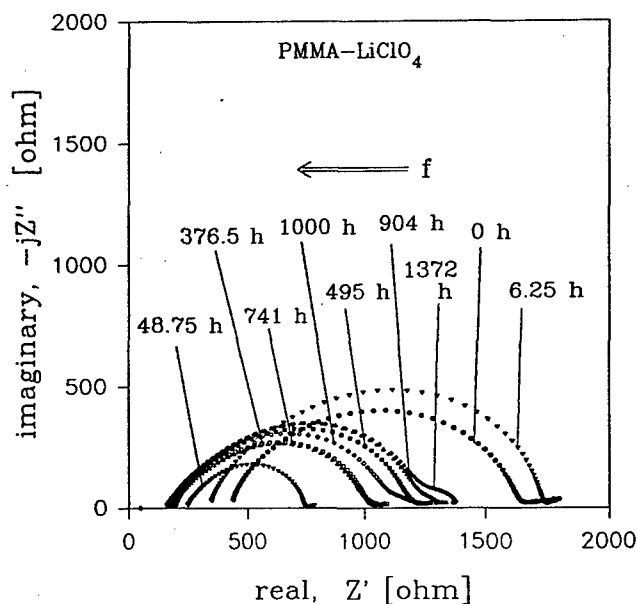


Figure 1- Time evolution of the impedance of a Li/PMMA-PC/EC-LiClO₄ (sample S-1) Li cell stored continuously under open circuit conditions at room temperature. The number of progressive hours of storage is indicated in the figure.

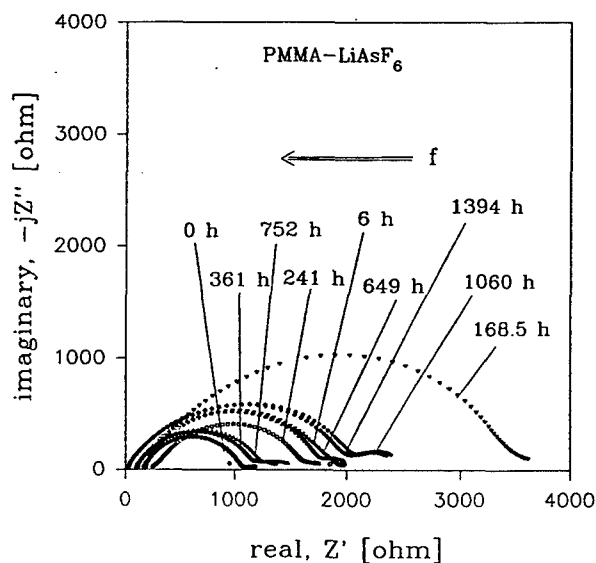


Figure 2- Time evolution of the impedance of a Li/PMMA-PC/EC-LiAsF₆ (sample S-2) Li cell stored continuously under open circuit conditions at room temperature. The number of progressive hours of storage is indicated in the figure.

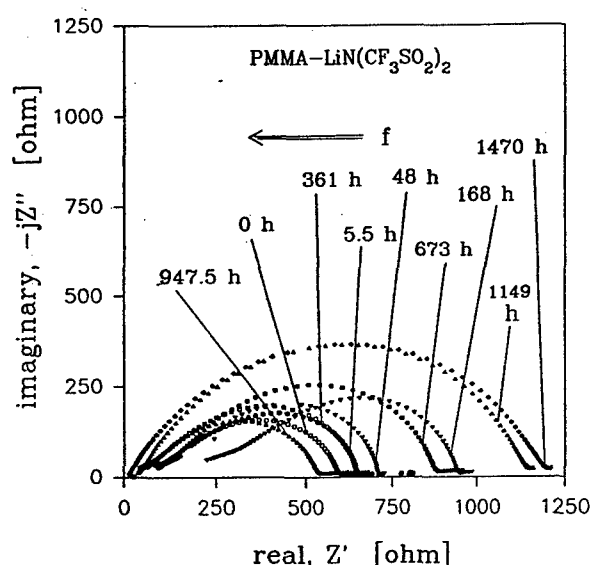


Figure 3- Time evolution of the impedance of a Li/PMMA-PC/EC
 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (sample S-3) Li cell stored continuously
 under open circuit conditions at room temperature.
 The number of progressive hours of storage is indicated in the
 figure.

Figures 1-3 illustrate the results obtained with the three electrolyte samples considered in this work. The related $-Z''$ - Z' plots reveal a progressive expansion of the middle frequency semicircle, an effect that in lithium cells may be typically attributed to interfacial phenomena. In fact, in these cells the expansion of the semicircle may be generally ascribed to a resistive layer continuously growing on the lithium electrode surface. Therefore, the expansion of the impedance semicircles of Figures 1-3 indicates that the lithium electrode is passivated when in contact with the PMMA-based gel electrolytes. On the other hand, this behaviour is not surprising since some of the electrolyte components, (i.e. EC and, particularly PC) are well known lithium corrosive agents.

However, one may notice that the expansion of the semicircles, and thus, the growth of the resistive layer, does not follow a regular trend but rather decreases during the initial time of contact. By using a model circuit which may be representative of the electrical equivalent of the lithium electrode interface, it is possible to separate the various impedance parameters which contribute to determine the evolutions illustrated by Figures 1-3. In this way one may represent the time evolution of the lithium interfacial resistances as reported in Figure 4. The trends clearly confirm that in all cases, but in

particular for cells based on the PMMA-LiAsF₆ electrolyte, after an initial sharp increase, the interfacial resistance decays, followed by a somewhat slower and irregular increase. One may tentatively explain this trend by assuming that the morphology of the passivation films evolves with time to finally acquire a non-compact, possibly porous structure. Obviously, this interpretation requires other support and further investigation should be carried out to substantiate the model of the lithium/PMMA-based electrolyte interface.

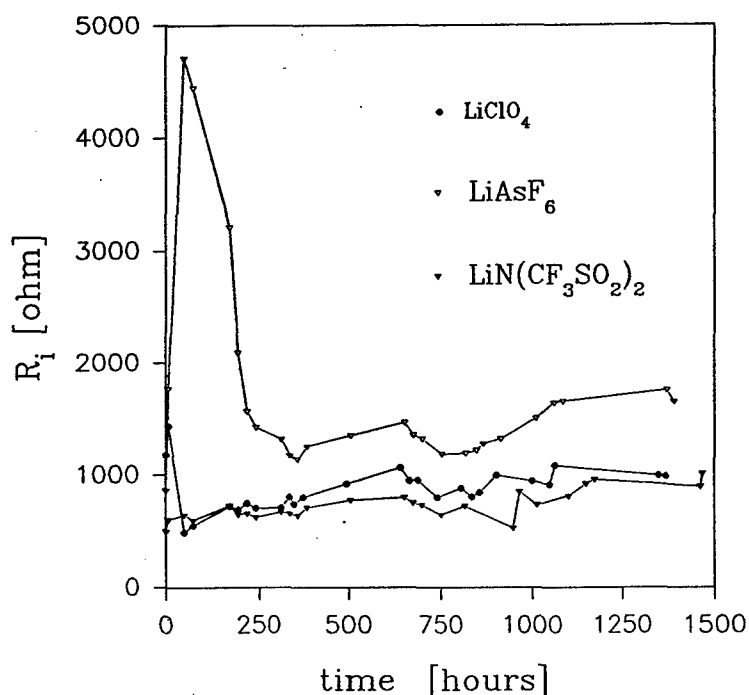


Figure 4 - Time evolution at 25 °C of the interfacial resistance R_i of the lithium electrode in the LiClO₄, EC/PC-PMMA, (sample S-1) LiAsF₆, EC/PC-PMMA (sample S-2) and LiN(CF₃SO₂)₂, EC/PC-PMMA (sample S-3) gel electrolytes under the conditions described in figures 1, 2, and 3, respectively.

However, from a purely qualitative point of view, one can state that in these PMMA electrolytes the growth kinetics of the lithium passivation layer is quite different from those observed in other gel-type media, as, for instance, in those based on PAN. Figure 5, which compares the time evolution of the lithium interfacial resistance in the two cases, clearly shows this difference: in the PAN-based cell the passivation occurs with a continuous growth and with a cumulative trend which becomes particularly dramatic as storage time increases and which is not even interrupted by occasional current drains; on the contrary, such a dramatic effect is not observed in the PMMA-based cell

and this certainly reflects some major differences on the kinetics and the cyclability of the lithium electrode in the two electrolyte media.

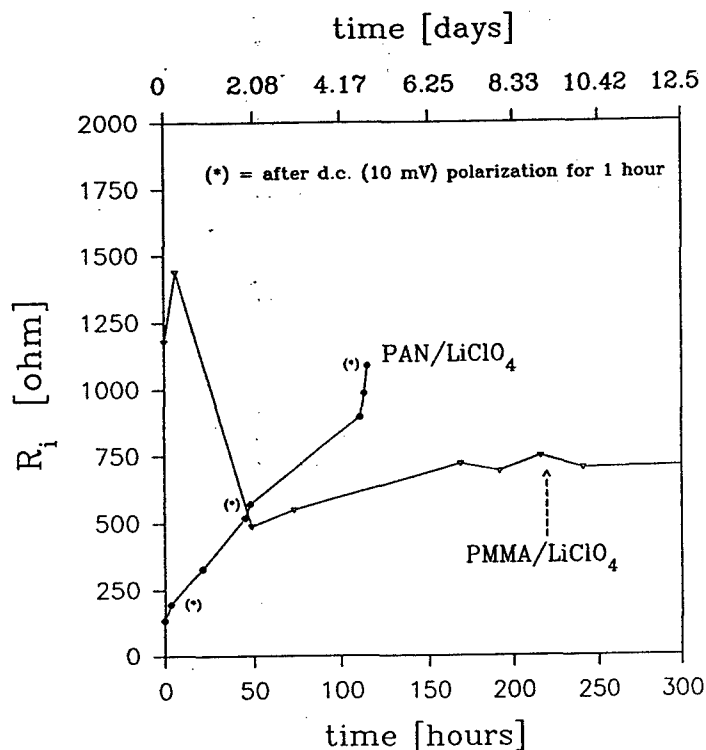


Figure 5 - Time evolution at 25 °C of the interfacial resistance R_i of the lithium electrode in the LiClO₄, EC/PC-PMMA and in the LiClO₄, EC/PC-PAN gel electrolytes.

Kinetics of the lithium plating-stripping process

The kinetics of the lithium deposition-stripping process:



from PMMA-based gel electrolytes on metal substrates (e.g., stainless-steel substrates) was determined by cyclic voltammetry. Figure 6 illustrates a typical result obtained in cells using PMMA-PC/EC-LiClO₄(sample S-1) electrolyte. A single cathodic deposition peak is followed by a single anodic stripping peak. The peak definition is good and the peak areas are comparable suggesting that the process is reversible, the kinetics are fast and the efficiency is high. However, the results of Figure 6 refer to a freshly made cell and thus, they are representative of the initial behaviour of the lithium electrode interface.

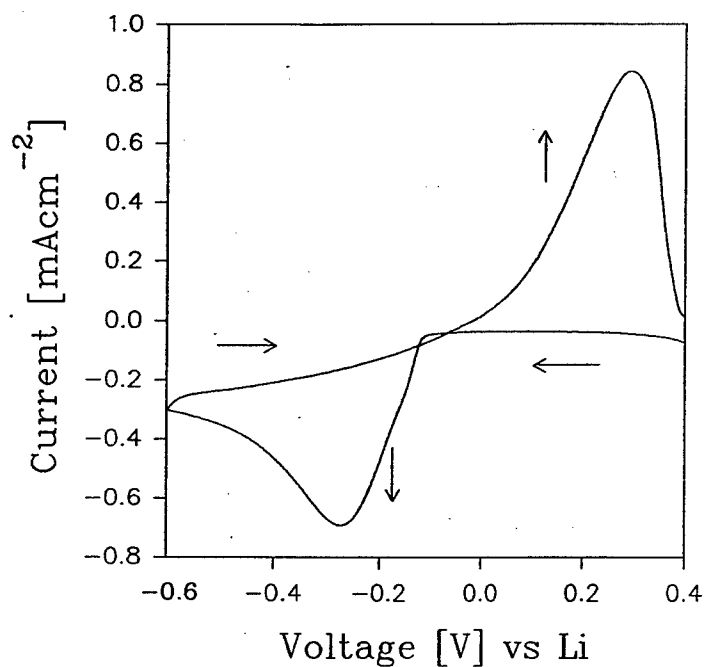


Figure 6- Cyclic voltammetry at 23 °C of the lithium plating-stripping process from a $\text{LiClO}_4\text{-EC/PC-PMMA}$ (sample S-1) electrolyte (freshly made cell) on a stainless-steel substrate. Lithium reference. Scan rate: 1 mVs^{-1} .

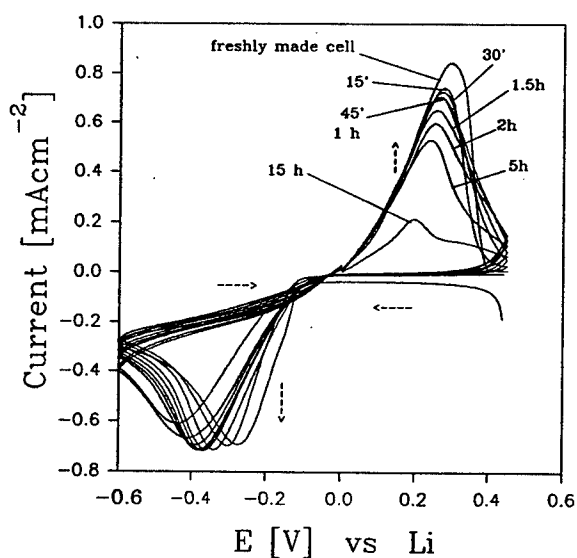


Figure 7- Cyclic voltammetry at 25 °C of the lithium plating-stripping process from a $\text{LiClO}_4\text{-EC/PC-PMMA}$ (sample S-1) electrolyte on a stainless-steel substrate run by allowing progressive time intervals (directly indicated in the figure) between the cathodic deposition peak and the anodic stripping peak. Lithium reference. Scan rate: 2 mVs^{-1} .

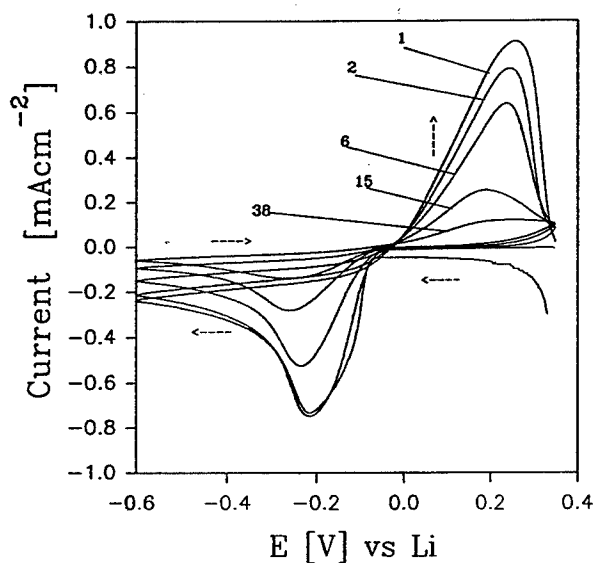


Figure 8- Cyclic voltammetry at 25 °C of the lithium plating-stripping process from a $\text{LiAsF}_6/\text{EC}/\text{PC}$ -PMMA (sample S-2) electrolyte on a stainless-steel substrate. The number of subsequent cycles are indicated in the figure. Lithium reference. Scan rate: 2 mVs^{-1} .

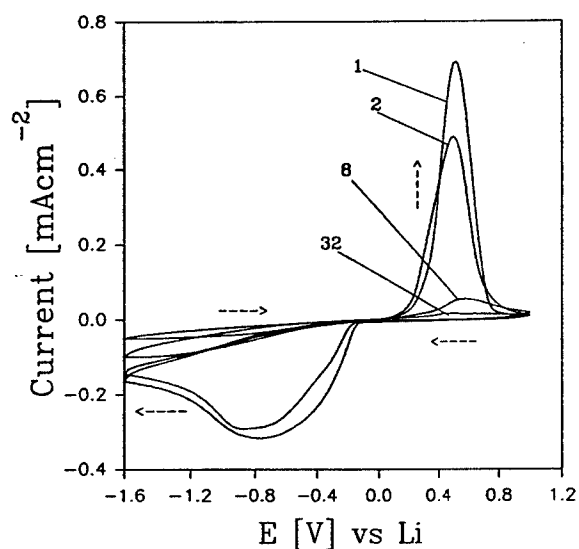


Figure 9- Cyclic voltammetry at 25 °C of the lithium plating-stripping process from a $\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{EC}/\text{PC}$ -PMMA (sample S-3) electrolyte on a stainless-steel substrate. The number of subsequent cycles are indicated in the figure. Lithium reference. Scan rate: 2 mVs^{-1} .

To investigate the effect of the corrosion phenomena at the lithium interface on a prolonged time scale, we have monitored the voltammetric response by allowing progressive time intervals between the cathodic deposition peak and the anodic stripping peak. Figure 7 illustrates the result: we notice that already after 15 minutes of delay time the recovery of lithium decreases and that it decays almost completely after 15 hours of storage. This suggests that, although to a lesser extent than in PAN-based media, the corrosion of the lithium electrode in PMMA-based electrolytes is still high enough to affect its cyclability. This is common to all three PMMA-LiX samples examined in this work, as demonstrated by the trends of repeated cyclic voltammograms carried out in the LiAsF_6 (sample S-2, Figure 8) and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (sample S-3, Figure 9) cases.

Efficiency of the lithium cycling process.

The conclusion reached in the previous session is of direct relevance for the applicability of the PMMA-based electrolytes and, therefore, we have attempted to investigate in greater details the cycling behavior of the lithium electrode in these electrolytes. Here we report some preliminary data on the cycling efficiency of the the lithium deposition-stripping processes in PMMA-based electrolyte cells. These data have been obtained by first depositing an excess of lithium on an "inert", stainless-steel substrate and then cycling a fraction of the deposited lithium until the overvoltage of the stripping process approached an infinite value.

The evolution upon cycles of this overvoltage for the three PMMA-LiX cells, is shown in Figure 10. The values of the related cycling efficiency E , obtained on the basis of equation (see previous 5th two-month Progress Report) :

$$E = \frac{Q_{\text{cycl}} - (Q_{\text{dep}}/n)}{Q_{\text{cycl}}}$$

are summarized in Table 1, where also data related to PAN-LiX cells are reported for comparison.

Conclusions.

The data of Table 1 confirm the expected improvement in lithium cyclability when passing from PAN-based to PMMA-based media (see also Fig. 4) and that, among these latter, the most efficient is sample S-3 which used the imide

salt (see Fig. 5). However, even in this case the efficiency, although promising, is still not sufficiently high to propose the PMMA-PC/EC $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ membrane as suitable electrolyte for long-life, rechargeable lithium batteries. As suggested by the voltammetric response (Fig. 7) and by the efficiency tests (Fig. 10) a consistent fraction of lithium is lost upon cycling and thus, that a large excess of lithium would eventually be required to assure an acceptable (e.g. greater than 500 cycles) life to the battery.

On the other hand these gel electrolyte membranes have unique and outstanding transport properties which motivates the present world-wide interest in their exploitation as high-energy battery separators. Therefore, further investigation with the objective of improving their interfacial stability with the lithium electrode is an important area to pursue. One possibility in this direction is based upon the addition of ceramic additives, an approach which in other cases have been shown to be quite effective in controlling lithium passivation phenomena (see Tab. 1). In addition, the effect of replacing one or both the organic solvent components, as well as the polymer host, should also be explored.

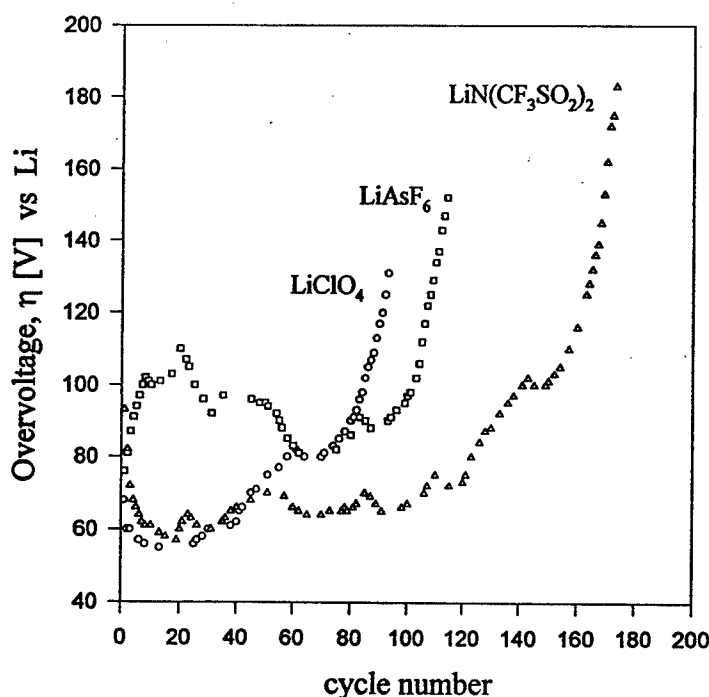


Figure 10- Evolution at 25 °C of the overvoltage η of the lithium stripping process upon cycling cells using the LiClO_4 , EC/PC, PMMA (sample S-1), the LiAsF_6 , EC/PC, PMMA (sample S-2), and the $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ EC/PC, PMMA (sample S-3) gel electrolyte, respectively.

Table 3-Efficiency of the lithium cycling process in gel electrolytes at 25 °C.
 $Q_{\text{dep}} = 0.5 \text{ C}$; $Q_{\text{cycl}} = 0.05 \text{ C}$.

electrolyte	sample	number of cycles, n	efficiency E (%)
PMMA-PC/EC/LiClO ₄	S-1	93	89
PMMA-PC/EC/LiAsF ₆	S-2	114	91
PMMA-PC/EC-LiN(CF ₃ SO ₂) ₂	S-3	173	94
PAN-PC/EC-LiClO ₄		18	72
PAN-PC/EC-LiClO ₄ + 10% zeolites		58	91